Retrograde Hydrate Phenomena at Low Pressures

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Abstract

A Gibbs free energy minimization technique has been applied to calculating phase equilibria of solid hydrates. The van der Waals and Platteeuw theory was used to predict the fugacity of water in each of the hydrate phases. Model parameters for ethane and propane were optimized to pure and binary incipient hydrate equilibrium data as well as to structural transition points for the ethane-propane-water system.

It is usually assumed that hydrates never dissociate with an increase in pressure. Predictions show, however, that for a wide water-free composition range, slight increases in pressure will result in the dissociation of sII hydrates (retrograde dissociation). Pressure versus temperature and pressure versus composition phase diagrams for the ethane-propane-water system showed that retrograde hydrate regions exist at low pressures (~10 to 15 atmospheres) near a temperature of 278 K. Retrograde hydrate regions were also predicted in the ethane-i-butane-water and ethane-propane-decane-water systems as well. Experiments were done to verify the model predictions for the ethane + propane + water system. Obtained hydrate dissociation data did not show a retrograde region. The possibility of a new hydrate structure forming instead warrants further investigation.

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Introduction

Gas hydrates are crystalline compounds that form when water molecules encage light hydrocarbons such as methane, ethane, and propane at high pressures and low temperatures. Hydrates are unusual in that the enclathrated gas molecules are not chemically bonded to the water lattice. The interaction between the guest molecule and the water lattice is of the van der Waals type.

Two different hydrate structures have been found to form from simple natural gases; structure I (sI) and structure II (sII). When in equilibrium with water, pure methane and pure ethane both form sI while pure propane and pure i-butane form sII. The hydrate structure formed from mixtures of these simple gases is sensitive to the composition of the gas mixture as well as the temperature and pressure of the system. This work discusses the predicted hydrate phase equilibria at and above the incipient formation conditions for mixtures of ethane, propane, i-butane, decane, and water at temperatures and pressures above and below incipient hydrate formation. Pressure and temperature measurements of hydrate formation conditions and Raman spectra have been obtained for the ethane-propane-water system to verify predictions.

Model

A multiphase flash routine based on the Gibbs energy minimization method of Bishnoi and Gupta [1] has been used in this work. The method is similar to that of Michelsen [2] and Avlonitis [3] in that it stems from the Gibbs energy tangent plane criterion. It can independently identify the phases present at equilibrium from information about pressure, temperature and composition. This prediction method has been widely used

for determining the amount of a phase present with increases in pressure and temperature. In this work, however, we have extended the use of the predictive method to generate pressure versus composition and pressure versus temperature plots for hydrates.

The possible phases included in the flash routine are vapor, liquid water, liquid hydrocarbon, sI hydrate, and sII hydrate. The Soave-Redlich-Kwong [4] equation of state is used to model fugacities in the vapor, liquid hydrocarbon, and liquid water phases. As an alternative to the SRK equation of state, the Krichevsky-Kasarnovsky [5] equation is used for the calculation of solubility of hydrocarbons in the liquid water phase.

The van der Waals and Platteeuw theory [6] is used to calculate hydrate fugacities. The governing equation that predicts the chemical potential of water in the hydrate lattice, $\boldsymbol{m}_v^H$ is

$$\boldsymbol{m}_W^H = \boldsymbol{m}_W^b + RT \sum_m \boldsymbol{u}_m \ln\left(1 - \sum_J \boldsymbol{q}_{Jm}\right) \tag{1}$$

where $\boldsymbol{m}_v^b$ is the chemical potential of water in the 'hypothetical' empty hydrate lattice, v_m is the number of cavities of type m per water molecule in the lattice, and $\boldsymbol{q}_{Jm}$ is the fractional occupancy of the Jth guest molecule in the mth hydrate cavity. This fractional occupancy can be expressed in a Langmuir type manner as

$$\boldsymbol{q}_{Jm} = \frac{C_{Jm} f_{Jm}}{1 + \sum_k C_{km} f_{km}} \tag{2}$$

where f_{Jm} and C_{Jm} are the fugacity and Langmuir constant of component J in cavity m. The Langmuir constants are temperature dependent functions that describe the potential

interaction between the encaged guest molecule and the water molecules surrounding it. They are evaluated by assuming a spherically symmetrical potential, which is described as

$$C_{Jm} = \frac{4\pi}{kT} \int_{0}^{R_m - a_J} \exp\left[-\frac{w_{Jm}(r)}{kT}\right] r^2 dr \tag{3}$$

where $w_{Jm}(r)$ is the cell potential function of guest J in cage m, R_m is the radius of cage m, and a_J is the spherical core radius of component J, respectively. In this work, the Kihara spherical core potential [7] is used to calculate water-guest interactions in each cage.

The chemical potential of water in the aqueous liquid derived from classical thermodynamics by Marshall et. al.[8], and simplified by Holder et. al. [9] and Menten et. al. [10], as

$$\mu_w^L = \mu_w^b - \Delta\mu_w^o \frac{T}{T_o} + RT \int_{T_o}^{T}\left(\frac{\Delta h_w}{RT^2}\right) dT - RT \int_{0}^{P}\left(\frac{\Delta v_w}{RT}\right) dP + RT \ln\left(a_w\right) \tag{4}$$

where $\Delta\mu_w^o$ is the difference in the chemical potential of water between the hypothetical empty hydrate lattice and liquid water at a reference temperature T_o (273.15 K) and zero absolute pressure, Δh_w and Δv_w are the enthalpy and volume differences between the empty hydrate and pure liquid water phases, and a_w is the activity of water.

To determine the fugacity of water in the hydrate phases, Equations 1 and 4 are used to obtain the expression,

$$f_w^H = f_w^{L_w} \exp\left(\frac{\mu_w^H - \mu_w^{L_w}}{RT}\right) \tag{5}$$

Note that the calculation of the hydrate fugacity depends on the chemical potential of water in the liquid water phase (Equation 4). Because of this, it is required that a liquid water

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phase be present. Therefore, all predictions with this algorithm must be with excess water present.

Experimental Setup

Research grade ethane and propane were obtained from Alphagaz. Distilled water from Nalgene was used. A 30/70 mol percent ethane/propane mixture was prepared using a gravimetric method. The balance used was a Sartorius balance with 0.01 gram precision.

A schematic of the experimental setup used in our experiments is given in Figure 1. The hydrates are formed in a brass high-pressure cell with two sapphire glass windows. This cell has an inner volume of approximately 3 cm^3 and is rated up to pressures of 350 atm. The cell temperature is regulated by circulating cooling fluid through the brass cell. A mixture of water and methanol was used as cooling fluid. A Haake A80 temperature bath was used to control the temperature of the cooling fluid. The temperature was measured using a thermocouple inserted in the brass block. The thermocouple was calibrated against a Fisher mercury thermometer.

The cell is filled with the prepared gas mixture of ethane and propane. The pressure in the cell is controlled by pumping distilled water into the cell, using a hand pump and was measured by a Heise pressure gauge. The errors in temperature and pressure measurements are smaller than 0.2 K and 0.3 atm, respectively.

Experimental procedure

At the start of the experiment, the ethane + propane gas mixture was charged into the cell and the pressure was set by compressing the gas with water. Hydrates were

initially formed by decreasing the temperature to the ice point. The hydrates formed as a very thin crust at the vapor-liquid interface. It should be noted that the cell was not stirred during the experiment.

The actual experiment was a slow heating of the equilibrium cell. Heating rates were less than 0.1 K per 5 minutes. The temperature and pressure at which the hydrate interface melted was noted down as the equilibrium condition. The procedure was then repeated at another pressure. When desired, a probe was connected to a Raman spectrometer and was used to obtain a Raman spectrum of the hydrate.

Modeling Results

Predictions have been made for the system ethane + propane + water. Figure 2 shows a predicted pressure versus water-free composition plot for this system at 274 K. At 0.0 mol fraction ethane (pure propane) sII will form at ~2 atm, and at 1.0 mol fraction ethane (pure ethane) sI will form at ~5 atm. At the intermediate composition of 0.75 mol fraction ethane, a quadruple point, L_w-sI-sII-V, will exist in which both hydrate structures exist in equilibrium with vapor and liquid water. This point will be referred to as the *structural transition composition*: the composition at which the incipient hydrate formation structure changes from sII to sI at a given temperature.

By Gibbs phase rule, there is only one pressure at which L_w-sI-sII-V can coexist. Therefore, with an increase in pressure, the free vapor phase is completely converted to either sI or sII, depending on the feed composition of ethane and propane and which hydrate structure is already present. This is illustrated in Figure 2. At pressures above

incipient hydrate formation phase regions are predicted to exist where both sI and sII hydrates are present.

Figure 2 illustrates the effect on hydrate formation when ethane and propane are combined at constant temperature. Ethane acts as an inhibitor to sII formation due to competition of ethane with propane to occupy the large cages of sII. Propane also acts as an inhibitor to sI formation when added to pure ethane. In this case, however, since propane cannot enter the sI cavities, the fugacity of ethane is diluted as propane is added, destabilizing the sI hydrate. Holder [11] refers to this inhibiting capacity as the "antifreeze" effect.

As the temperature is increased to 277.9 K the pressure versus composition diagram for the ethane-propane-water system changes drastically as shown in Figure 3. Between 0.0 and 0.5 mol fraction of ethane, the incipient hydrate structure is sII hydrate. However, if the pressure is increased to approximately 9.5 atm, between 0.23 and 0.5 mol fraction ethane, sII is predicted to dissociate to form a L_w-V-L_{hc} region. The pressure at which this dissociation is predicted to occur is called the *hydrate retrograde pressure* at T, analogous to the phenomena of vapor-liquid retrograde regions [12].

The retrograde pressure can be explained via evaluation of the vapor-liquid equilibria of the ethane, propane, and water. The dashed line in Figure 3 is L_w-V-L_{hc} envelope that would form if hydrates were not present. The L_w-sII-V phase region intersects the L_w-V-L_{hc} region at the quadruple point (9.5 atm). This point of intersection is a four-phase point, L_w-sII-V-L_{hc}, and according to Gibbs phase rule there is one degree of freedom (3 components, 4 phases), namely temperature which is set at 277.9 K. This means that, in Figure 3, the pressure at which the quadruple point occurs is unique.

Therefore, if pressure is increased, one of the phases must disappear. In this case, the sII phase dissociates and a L_w-V-L_{hc} region remains.

The validity of the predictions in Figure 3 can be shown with a comparison of the data taken by Holder and Hand [13] for this system. The sII incipient hydrate formation data point at 0.28 mol fraction ethane compares quite well with the predictions. Holder and Hand state that the data point at 0.68 mol fraction is sI but note that it could be at L_w-sI-V-L_{hc} conditions. The predictions in Figure 3 support their observation of a quadruple point.

A similar system to ethane-propane-water is ethane-i-butane-water in that pure ethane forms sI while pure i-butane forms sII. A retrograde phenomenon is also predicted to occur in this system as shown in the pressure versus water-free composition diagram at 275.15 K in Figure 4. Note that the temperature at which the retrograde phenomenon occurs is lower than in the ethane-propane-water system due to the low vapor pressure of i-butane.

We hypothesize that retrograde phenomena will occur in any binary system in which sI and sII formers that have fairly low vapor pressures are present (due to Gibbs phase rule). Predictions show that the retrograde phenomenon will not occur in systems in which a significant amount of methane is present since methane is well above its critical point. However, predictions also show that the retrograde phenomena are not constrained to binary systems.

Retrograde phenomena are predicted to occur in multi-component systems as well. Figure 5 is a water-free phase amount versus pressure diagram for the ethane-propane-decane-water system at 277.5 K. Note that the amount of water in the system is not displayed since all predictions are made with excess water. The top portion of the figure

shows the phases present in a specified pressure range. That is, between 1 atm and 6.5 atm, liquid water, vapor, and liquid hydrocarbon are present. At 6.5 atm sII hydrates form. As pressure is increased, the amount of sII increases. As this is occurring, the vapor phase is being depleted of light components (ethane and propane) and the liquid hydrocarbon phase is increasing due to the increase in pressure (condensation of vapor).

The amount of sII in the system is predicted to reach a maximum amount at ~8 atm. The sII hydrates then start to dissociate as pressure is increased, completely dissociating at ~9.6 atm. After sII dissociates, there is a small pressure window in which L_w-V-L_{hc} are present (9.6-10 atm). The only phases predicted to be present at pressures greater than 10 atm are liquid water and liquid hydrocarbon. Note that the retrograde phenomenon in this system cannot be explained by Gibbs phase rule since the system has more than one degree of freedom at the four-phase condition.

Experimental Results

Experiments have been conducted to support model predictions at a gas composition of 30 mol percent ethane and 70 mol percent propane. A pressure versus temperature diagram was predicted using the model and is shown in Figure 6. The lines are model predictions and the circles are experimental observations of hydrate dissociation. Retrograde phenomena are predicted to occur between the temperatures of 277.7 K and 278.3 K. With a pressure increase of up to 5 atmospheres sII hydrates will dissociate at any temperature in this range.

As can be seen in Figure 6, the incipient hydrate formation data obtained does not suggest retrograde melting. The predictions compare well with the data for temperatures up

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to the quadruple point, L_w-sII-V-L_{hc} (278.3 K, 7.3 atm). However, the data imply that the hydrate stability region extends to 279 K, instead of showing retrograde dissociation. Note that the uncertainty in the data is quite large in the region where sII hydrates dissociate to both vapor and liquid hydrocarbon phases (i.e. for pressures between 7.3 and 11 atm).

To verify the structure of the hydrates formed, several Raman spectra of the hydrates have been obtained at temperatures and pressures throughout the phase diagram. It was found that all hydrates below the quadruple point are structure II, with mainly propane occupying the large cavity, as the predictions suggest. Some of the spectra measured above the quadruple point are anomalous and are still being investigated.

Discussion of Results

The differences between the predicted and the observed phase equilibria of the ethane-propane-water system could have several explanations:

      (1) model parameters are incorrect.

      (2) kinetics may limit retrograde phenomena.

      (3) a new hydrate structure.

It is not probable that incorrect model parameters are the cause for such large discrepancies. Predictions at temperatures below the quadruple point in Figure 6 compare very well with the data. In fact, predictions qualitatively compare well with the complete set of hydrate data for all systems (i.e. if predictions do not quantitatively compare well, the general trend of the data is still predicted well). In this case, however, the general trend of the data is quite different than that of the predictions.

It is also not likely that retrograde phenomena are limited by kinetics. If kinetics were limiting the process, it would be expected that the data would not have a general trend, as it does in Figure 6. To test this, we held the system at 278 K and 15 atm for 24 hours (conditions at which hydrates are not stable according to predictions). No dissociation was observed. Also hydrate melting kinetics are expected to be fast, given that this is a transition from an ordered (hydrate) to a less ordered state (liquid hydrocarbon).

The appearance of a new hydrate structure in the regions in which the data and predictions differ would explain the data and anomalous spectra we have obtained. A new hydrate structure would not be predicted by the model, since it can only predict sI and sII hydrates.

Conclusions

Retrograde phenomena have been predicted using a Gibbs energy minimization model using the van der Waals and Platteeuw theory of natural gas hydrates. The phenomena are predicted to occur in systems containing ethane, propane, i-butane, decane, and water. Experiments have been performed for the ethane (30 mol%), propane (70 mol%), and water system to verify the predictions. It was found that experimental data does not show retrograde phenomena. In further research we will investigate the possibility of a new hydrate structure being present in the region where retrograde phenomena are predicted to occur for this particular system.

List of Symbols

Symbol	Description
R	gas constant, hydrate cage radius (Å)
T	temperature (Kelvin)
C	Langmuir constant
f	fugacity
k	Boltzmann's constant (J/K)
r	integration variable
a	guest core radius, activity
h	enthalpy (J/mol-K)
v	molar volume (cm^3/mol)
P	pressure

Greek Letters

μ	chemical potential (J/mol)
υ	number of hydrate cavities per water molecule
θ	fractional occupancy of guests in the hydrate cages, stability variable
$w(\ )$	cell potential function
Δ	difference between empty hydrate lattice and liquid water

Subscripts

J	hydrate guest component
m	hydrate cavity
w	water
o	property at reference conditions (also superscript)

Superscripts

β	empty hydrate lattice phase
H	hydrate phase
L	liquid water phase

Acknowledgements

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Figure Captions

Figure 1. Experimental apparatus and setup used for phase equilibria measurements.

Figure 2. Pressure versus water-free composition diagram for ethane-propane-water system at 274 K.

Figure 3. Pressure versus water-free composition diagram for ethane-propane-water system at 277.9 K.

Figure 4. Pressure versus water-free composition diagram for ethane-i-butane-water system at 275.15 K.

Figure 5. Water-free phase amount versus pressure diagram for ethane(0.2667)-propane(0.6857)-decane(0.0476)-water(excess) system at 277.5 K.

Figure 6. Pressure versus temperature diagram for ethane (0.3)-propane (0.7)-water (excess) system.

Gas Reservoir

Pressure
Gauge

P

T

Hand Pump

Drain

Temperature bath

~T

Probe

To spectrometer

Pressure (atm)

30

25

20

15

10

5

0

L_w-sII

L_w-sII-L_{hc}

L_w-L_{hc}

L_w-sI-L_{hc}

L_w-V-L_{hc}

L_w-sI-V

L_w-sII-V

L_w-V

○ Holder and Hand, 1982

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7   0.8   0.9   1

Mole Fraction Ethane

L_w-V-L_{hc} L_w-sII-V-L_{hc} L_w-V-L_{hc} L_w-L_{hc}

Vapor
Liquid Hydrocarbon
sII Hydrate

Water-free Phase Amount

Pressure (atm)